Synthesis of Novel Bio-Derived Polyesters Through the Development of New Electron Deficient Palladium Catalyst

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Introduction

- Carbonylation [1] reactions of alkenes constitute the most important industrial processes in homogeneous catalysis. State-of-the-art phosphine ligands reported by Mecking et al.[3] and Beller et al.[4] display the use of various electron rich ligands in applications ranging from hydroesterifications[1] to carbonylation polymerizations[3].

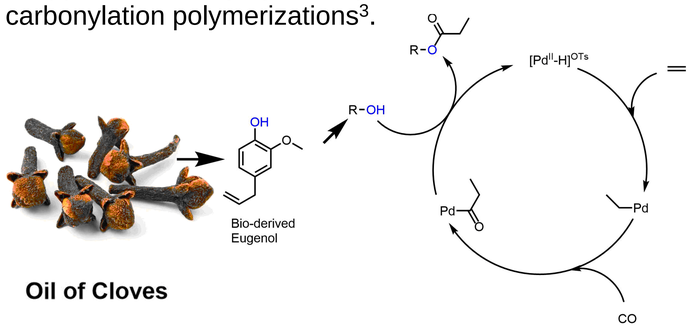
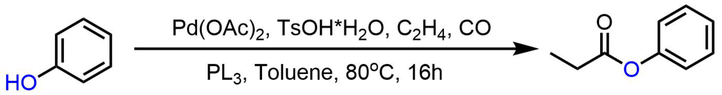


Figure 1. Phosphine ligands used in hydroesterifications of phenol and eugenol

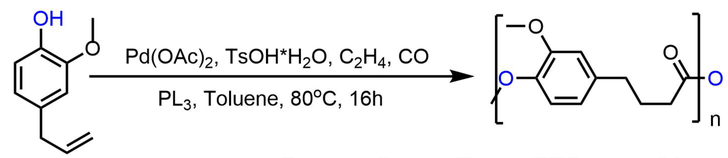
- One of the goals for this project consisted of using eugenol, a bio-derived terpenoid, as a substrate for a potential polymerization.

Experimental

- In order to test effects of various ligands on conversion of phenol, the following setup was used:



- Next, sterically different eugenol was used as a substrate with a similar set of phosphine ligands:



- Reactions were carried in Fischer-Porter Tube (FTP) with 80 psi ethylene/160 psi CO partial pressures. FTP setup illustrated below:

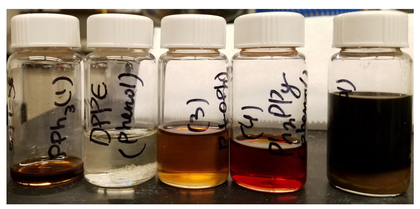


Figure 2. FTP reactor (LEFT) with hydroesterification products (RIGHT)

Hydroesterification of Phenol

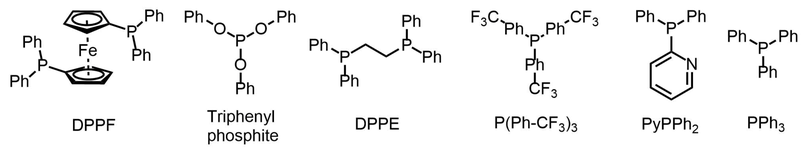


Figure 3. Phosphine ligands used in hydroesterifications of phenol and eugenol

- Among above ligands, both PPh_3 and $P(Ph\text{-}CF_3)_3$ yielded the highest (~90-95%) conversion of phenol into ester as was determined by GC.
- Phenol is a decent nucleophile for hydroesterification reactions involving CO and ethylene.
- Bi-dentate ligands likely compete with ethylene/CO co-polymerization, a phenomenon well supported in a literature.

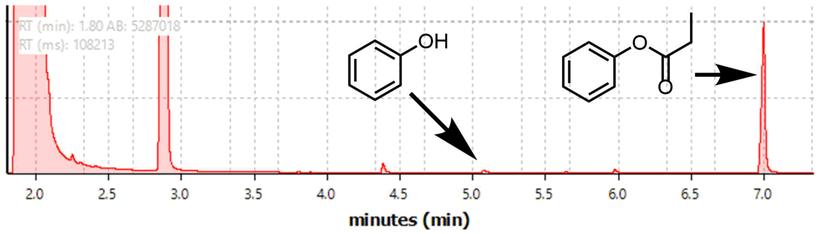


Chart 1. GC-FID retention times for hydroesterification of phenol using PPh_3

Hydroesterification of Eugenol

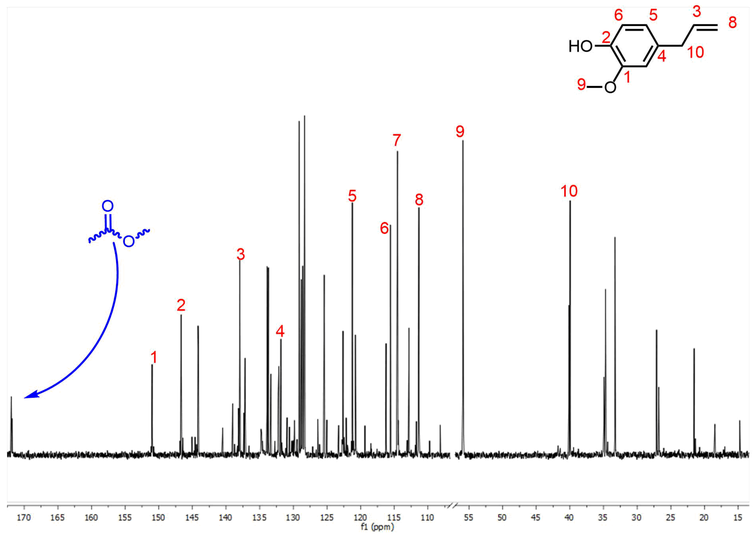
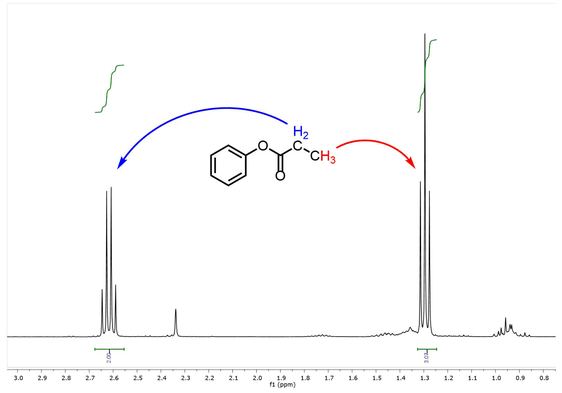


Chart 2. ^{13}C NMR peaks of hydroesterified eugenol with carbonyl peak shown in BLUE

Conclusions

- A relatively high conversion (~ 90-95% by GC-FID Arc) of phenol into a phenyl propanoate was achieved using PPh_3 and $P(Ph\text{-}CF_3)_3$, as well as using DPPF.



- In reaction of eugenol with PPh_3 – an ester was formed. An evidence of hydroesterification of eugenol.

Future Work

- We plan to investigate effects of steric hinderance in eugenol on reaction rate
- We plan to study terminal olefin affinity towards a palladium-olefin adduct formation.

Acknowledgements

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References

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